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### (54) Detergent tablet with high dissolution and mechanical characteristics

(57) The present invention relates to a tablet formed by compressing a particulate material, the particulate material comprising a surfactant and a hydrotrope compound, the hydrotrope compound having a cohesive effect on the particulate material.

In a further aspect of the invention there is provided a tablet for preparing an aqueous solution of a laundry detergent having a tensile strength of at least 15 kPa, the tablet giving less than 40% per weight residue in the

dispenser at the end of the water supply cycle under dispensing test, the dispensing test consisting of two tablets, each tablet weighing 50g, being placed in the dispenser of a Baucknecht® WA9850 washing machine, the water supply to the washing machine being set at a temperature of 20°C and a hardness of 21 grains per gallon, the dispenser water inlet flow rate being set to 8 l/min, the machine being set to program 4 (white/colors, short cycle) and switched on.

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## Description

[0001] The present invention relates to detergent tablets, especially those adapted for use in washing.

[0002] Although cleaning compositions in tablet form have often been proposed, these have not (with the exception of soap bars for personal washing) gained any substantial success, despite the several advantages of products in a unit dispensing form. One of the reasons for this may be that detergent tablets usually dissolve slower than the constituent powders from which they are made, simply because the constituent powders are forced close together in the tablet, with comparatively little opportunity for water to permeate between them. This gives rise to the problem that slow dissolving tablets cause residues which may for example be visible through the door of the washing machine during the wash cycle, or which stick to the fabrics at the end of the wash cycle, or both.

[0003] EP-A-0 711 827, published on the 5<sup>th</sup> of May 1996, discloses laundry detergent tablets containing a highly water-soluble material which improves disintegration of the whole tablet and dissolution of its soluble ingredients.

[0004] However, particularly in certain front loading washing machines, problems of tablet residues appearing visibly at the window of the washing machine have still been encountered.

[0005] The object of the present invention is to provide tablets formed by compressing a particulate material, the particulate material comprising a surfactant, the tablet being suitable for storing, shipping and handling without breakage while dissolving easily and rapidly in wash solution, releasing the active ingredients into the wash solution and completely disintegrating and dispersing in alkaline or surfactant-rich solutions such as the wash liquor.

## Summary of the Invention

[0006] The object of the invention is achieved by providing a tablet of the above mentioned kind, whereby the particulate material further comprises a hydrotrope compound, the hydrotrope compound having a cohesive effect on the particulate material.

[0007] In a further aspect of the invention there is provided a tablet having a tensile strength of at least 15 kPa for preparing an aqueous solution of a laundry detergent, the tablet giving less than 40% per weight residue in the dispenser at the end of the water supply cycle under dispensing test, the dispensing test consisting of two tablets, each tablet weighing 50g, being placed in the dispenser of a Baucknecht® WA9850 washing machine, the water supply to the washing machine being set at a temperature of 20°C and a hardness of 21 grains per gallon, the dispenser water inlet flow rate being set to 8 l/min, the machine being set to program 4 (white/colors, short cycle) and switched on.

[0008] In a further aspect of the invention a method is provided of preparing an aqueous solution of a laundry detergent for use in a washing machine, wherein the aqueous solution of laundry detergent is formed by dissolving in water a tablet formed by compressing a particulate material, the tablet comprising a surfactant and a hydrotrope compound, the hydrotrope compound having a cohesive effect on the particulate material.

## Detailed Description of the Invention

[0009] The invention relates to a hydrotrope compound having a cohesive effect on the particulate material.

## Hydrotrope Compounds

[0010] For the purpose of the invention, a specific compound is defined as being hydrotrope as follows (see S.E. Friberg and M. Chiu, J. Dispersion Science and Technology, 9(5&6), pages 443 to 457, (1988-1989)):

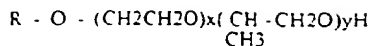
1. A solution is prepared comprising 25% by weight of the specific compound and 75% by weight of water.
2. Octanoic Acid is thereafter added to the solution in a proportion of 1.6 times the weight of the specific compound in solution, the solution being at a temperature of 20° Celsius. The solution is mixed in a Sotax beaker with a stirrer with a marine propeller, the propeller being situated at about 5mm above the bottom of the beaker, the mixer being set at a rotation speed of 200 rounds per minute.
3. The specific compound is hydrotrope if the the Octanoic Acid is completely solubilised, i.e. if the solution comprises only one phase, the phase being a liquid phase.

[0011] It should be noted that in a preferred embodiment of the invention, the hydrotrope compound is a flowable material made of solid particles at operating conditions between 15 and 60° Celsius for ease of handling, but other forms may be used such as a paste or a liquid.

Hydrotrope compounds include the compounds listed thereafter:

A list of commercial hydrotropes could be found in McCutcheon's Emulsifiers and Detergents published by the McCutcheon division of Manufacturing Confectioners Company. Compounds of interest also include:

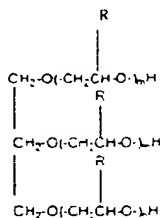
1. Nonionic hydrotrope with the following structure:



where R is a C<sub>8</sub>-C<sub>10</sub> alkyl chain, x ranges from 1 to 15, y from 3 to 10.

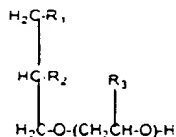
2. Anionic hydrotropes such as alkali metal aryl sulfonates. This includes alkali metal salts of benzoic acid, salicylic acid, benzenesulfonic acid and its many derivatives, naphthoic acid and various hydroaromatic acids. Examples of these are sodium, potassium and ammonium benzene sulfonate salts derived from toluene sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, tetralin sulfonic acid, naphthalene sulfonic acid, methyl- naphthalene sulfonic acid, dimethyl naphthalene sulfonic acid, trimethyl naphthalene sulfonic acid= Other examples include salts of dialkyl benzene sulfonic acid such as salts of di-isopropyl benzene sulfonic acid, ethyl methyl benzene sulfonic acid, alkyl benzene sulfonic acid with an alkyl chain length with 3 to 10, (pref. 4 to 9), linear or branched alkyl sulfonates with an alkyl chain with 1 to 18 carbons.

3. Solvent hydrotropes such as alkoxyated glycerines and alkoxyated glycerides, esters alkoxyated glycerines, alkoxyated fatty acids, esters of glycerin, polyglycerol esters. Preferred alkoxyated glycerines have the following structure:



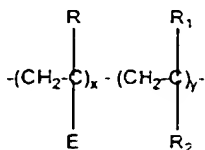
where l, m and n are each a number from 0 to about 20, with l+m+n = from about 2 to about 60, preferably from about 10 to about 45 and R represents H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>

Preferred alkoxyated glycerides have the following structure



where R<sub>1</sub> and R<sub>2</sub> are each C<sub>n</sub>COO or -(CH<sub>2</sub>CHR<sub>3</sub>-O)<sub>l</sub>-H where R<sub>3</sub> = H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> and l is a number from 1 to about 60, n is a number from about 6 to about 24.

4. Polymeric hydrotropes such as those described in EP636687:



where

E is a hydrophilic functional group,

R is H or a C1-C10 alkyl group or is a hydrophilic functional group;

R1 is H or a lower alkyl group or an aromatic group,

R2 is H or a cyclic alkyl or aromatic group.

The polymer typically has a molecular weight of between about 1000 and 1000000.

5. Hydrotrope of unusual structure such as 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (Diacid®)

Such a hydrotrope compound could be formed from a mixture or from a single compound.

#### Cohesive Effect

**[0012]** For the purpose of this invention, the Cohesive Effect on the particulate material of a detergent matrix is characterised by the force required to break a tablet based on the examined detergent matrix pressed under controlled compression conditions. For a given compression force, a high tablet strength indicates that the granules stuck highly together when they were compressed, so that a strong cohesive effect is taking place. Means to assess tablet strength (also refer to diametrical fracture stress) are given in Pharmaceutical dosage forms: tablets volume 1 Ed. H.A. Lieberman et al, published in 1989.

The stickiness induced by the hydrotrope compound is measured according to the invention by comparing the tablet strength of the original base powder without hydrotrope with the tablet strength of a powder mix which comprises 97 parts of the original base powder and 3 parts of hydrotropes. The hydrotrope is added to the matrix in a form in which it is substantially free of water (water content below 10% (pref. below 5%)). The temperature of the addition is between 10 and 80°C, more pref. between 10 and 40°C.

A hydrotrope compound is defined as having a cohesive effect on the particulate material according to the invention when at a given compacting force of 3000N, tablets with a weight of 50g of detergent particulate material and a diameter of 55mm have their tablet tensile strength increased by over 30% (preferably 60 and more preferably 100%) by means of the presence of 3% of the hydrotrope compound having a cohesive effect in the base particulate material.

**[0013]** It was found that when integrating a hydrotrope compound having a cohesive effect on the particulate material according to the invention to a tablet formed by compressing a particulate material comprising a surfactant, the dissolution of the tablet in an aqueous solution was significantly increased. In a preferred embodiment, at least 1% per weight of the tablet is formed from the hydrotrope compound, more preferably at least 2%, even more preferably at least 3% and most preferably at least 5% per weight of the tablet being formed from the hydrotrope compound having a cohesive effect on the particulate material.

It should be noted that a composition comprising a hydrotrope compound as well as a surfactant is disclosed in EP-A-0 524 075, this composition being a liquid composition.

According to the present invention it was found that the hydrotrope compound having a cohesive effect on the particulate material allows to obtain a tablet having a higher tensile strength at constant compacting force or an equal tensile strength at lower compacting force when compared to traditional tablets. Typically, the tablet will have a tensile strength of more than 5kPa, preferably of more than 10kPa, more preferably, in particular for use in laundry applications, of more than 15kPa, even more preferably of more than 30 kPa and most preferably of more than 50 kPa, in particular for use in dish washing or auto dish washing applications; and a tensile strength of less than 300 kPa, preferably of less than 200 kPa, more preferably of less than 100 kPa, even more preferably of less than 80 kPa and most preferably of less than 60 kPa. Indeed, in case of laundry application, the tablets should be less compressed than in case of auto dish washing applications for example, whereby the dissolution is more readily achieved, so that in a laundry application, the tensile strength is preferably of less than 30 kPa.

This allows to produce tablets which have a solidity and mechanical resistance comparable to the solidity or mechanical resistance of traditional tablets while having a less compact tablet thus dissolving more readily. Furthermore, as the compound is hydrotrope, the dissolution of gelling material such as surfactant is further facilitated, resulting in a synergy leading to facilitated dissolution for a tablet according to the invention.

#### Highly soluble Compounds

**[0014]** In a preferred embodiment of the invention, the hydrotrope compound having a cohesive effect is a highly soluble compound. Such a compound could be formed from a mixture or from a single compound. A highly soluble compound is defined as follows:

A solution is prepared as follows comprising de-ionised water as well as 20 grams per litre of a specific compound:

1- 20 g of the specific compound is placed in a Sotax Beaker. This beaker is placed in a constant temperature bath set at 10°C. A stirrer with a marine propoeller is placed in the beaker so that the bottom of the stirrer is at 5 mm above the bottom of the Sotax beaker. The mixer is set at a rotation speed of 200 turns per minute.

- 2- 980 g of the deionised water is introduced into the Sotax beaker.
- 3- 10 s after the water introduction, the conductivity of the solution is measured, using a conductivity meter.
- 4- Step 3 is repeated after 20, 30, 40, 50, 1min, 2 min, 5 min and 10 min after step 2.
- 5- The measurement taken at 10 min is used as the plateau value or maximum value.

**[0015]** The specific compound is highly soluble according to the invention when the conductivity of the solution reaches 80% of its maximum value in less than 10 seconds, starting from the complete addition of the de-ionised water to the compound. Indeed, when monitoring the conductivity in such a manner, the conductivity reaches a plateau after a certain period of time, this plateau being considered as the maximum value. Such a compound is preferably in the form of a flowable material constituted of solid particles at temperatures comprised between 10 and 80°Celsius for ease of handling, but other forms may be used such as a paste or a liquid. Example of highly soluble compounds include Sodium di isoalkylbenzene sulphonate or Sodium toluene sulphonate.

#### Tablet Manufacture

**[0016]** The invention allows to obtain a less compact and less dense tablet at constant compacting force when compared to a traditional detergent tablet.

Detergent tablets of the present invention can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

In particular for laundry tablets, the ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet suitable for laundry compressed using a force of less than 2500N, but tablets for auto dish washing may also be considered for example, whereby such auto dish washing tablets are usually more compressed than laundry tablets.

The detergent tablets can be made in any size or shape and can, if desired, be coated and even surface treated before coating. The tablet includes a surfactant which normally provides a substantial part of the cleaning power of the tablet and preferably also a builder. The term "builder" is intended to mean all materials which tend to remove calcium ion from solution, either by ion exchange, complexation, sequestration or precipitation. The term "surfactant" is intended to mean all material which tend to reduce the surface tension of water when in solution.

The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tableting, briquetting, or extrusion, preferably tableting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m<sup>2</sup>, preferably not exceed 30000 kN/m<sup>2</sup>, more preferably not exceed 5000 kN/m<sup>2</sup>, even more preferably not exceed 3000kN/m<sup>2</sup> and most preferably not exceed 1000kN/m<sup>2</sup>. In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

## Coating

[0017] Solidity of the tablet according to the invention may be further improved by making a coated tablet, the coating covering a non-coated tablet according to the invention, thereby further improving the mechanical characteristics of the tablet while maintaining or further improving dissolution.

In one embodiment of the present invention, the tablets may then be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dissolved under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of undissolved particles or lumps of coating material on the laundry load.

Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

Suitable coating materials are dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof.

The coating material has a melting point preferably of from 40 °C to 200 °C.

The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40 °C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200 °C are not practicable to use. Preferably, the materials melt in the range from 60 °C to 160 °C, more preferably from 70 °C to 120 °C.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

The tablet coatings of the present invention are very hard and provide extra strength to the tablet.

In a preferred embodiment of the present invention the fracture of the coating in the wash is improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dissolution of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose Sodium, crospovidone, cellulose, carboxymethyl cellulose, alginic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysaccharides, ion exchange resins and mixtures thereof.

## Tensile Strength

[0018] Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape. For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet, and is determined by the following equation :

$$= \frac{2 F}{\mu D t}$$

Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet, and t the thickness of the tablet. (Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217). A tablet having a diametral fracture

stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

#### Tablet Dispensing

**[0019]** The rate of dispensing of a detergent tablet can be determined in the following way:

Two tablets, nominally 50 grams each, are weighed, and then placed in the dispenser of a Baucknecht® WA9850 washing machine. The water supply to the washing machine is set to a temperature of 20 °C and a hardness of 21 grains per gallon, the dispenser water inlet flow-rate being set to 8 l/min. The level of tablet residues left in the dispenser is checked by switching the washing on and the wash cycle set to wash program 4 (white/colors, short cycle). The dispensing percentage residue is determined as follows:

$$\% \text{ dispensing} = \text{residue weight} \times 100 / \text{original tablet weight}$$

The level of residues is determined by repeating the procedure 10 times and an average residue level is calculated based on the ten individual measurements. In this stressed test a residue of 40 % of the starting tablet weight is considered to be acceptable. A residue of less than 30% is preferred, and less than 25% is more preferred.

It should be noted that the measure of water hardness is given in the traditional "grain per gallon" unit, whereby 0.001 mole per litre = 7.0 grain per gallon, representing the concentration of Ca<sup>2+</sup> ions in solution.

#### Effervescent

**[0020]** In another preferred embodiment of the present invention the tablets further comprises an effervescent.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,



Further examples of acid and carbonate sources and other effervescent systems may be found in: (Pharmaceutical Dosage Forms: Tablets Volume 1 Page 287 to 291).

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dissolution aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dissolution aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H.A. Lieberman et al, ISBN 0-8247-8044-2.

#### Detergent surfactants

**[0021]** Surfactant are comprised in the tablet according to the invention. The dissolution of surfactants is favoured by the addition of the hydrotrope compound.

Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C<sub>10</sub>-C<sub>20</sub> alkyl sulfates ("AS"), the C<sub>10</sub>-C<sub>18</sub> secondary (2,3) alkyl sulfates of the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub>(CHOSO<sub>3</sub>M<sup>+</sup>)CH<sub>3</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>y</sub>(CHOSO<sub>3</sub>M<sup>+</sup>)CH<sub>2</sub>CH<sub>3</sub> where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AES"; especially EO 1-7 ethoxy sulfates), C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C<sub>10</sub>-C<sub>18</sub> glycerol ethers, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, and C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such

as the C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and the like, can also be included in the overall compositions. The C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides can be used for low sudsing. C<sub>10</sub>-C<sub>20</sub> conventional soaps may also be used. If high sudsing is desired, the branched-chain C<sub>10</sub>-C<sub>16</sub> soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts. In a preferred embodiment, the tablet comprises at least 5% per weight of surfactant, more preferably at least 15% per weight, even more preferably at least 25% per weight, and most preferably between 35% and 45% per weight of surfactant. In case of use for dish washing applications, lower levels of surfactant may be considered, i.e. preferably levels of at least 2% per weight.

#### Non gelling binders

**[0022]** Non gelling binders can be integrated to the particles forming the tablet in order to further facilitate dissolution. If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet. It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

#### Builders

**[0023]** Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition.

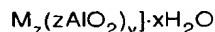
Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. Examples of silicate builders are the alkali metal silicates, particularly those having a SiO<sub>2</sub>:Na<sub>2</sub>O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na<sub>2</sub>SiO<sub>5</sub> morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi<sub>x</sub>O<sub>2x+1</sub>·yH<sub>2</sub>O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na<sub>2</sub>SiO<sub>5</sub> (NaSKS-6 form) is most preferred for use herein. Other silicates may also



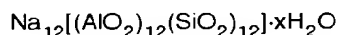
be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2.321.001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxy-disuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator. In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-

laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

## Bleach

**[0024]** The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundrying. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetrahydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxydecanoic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

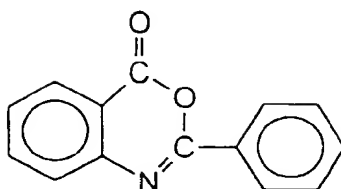
Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

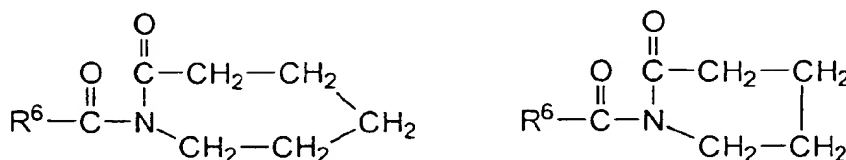
Highly preferred amido-derived bleach activators are those of the formulae:



wherein  $R^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $R^2$  is an alkylene containing from 1 to about 6 carbon atoms,  $R^5$  is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate. Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference. Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein  $R^6$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate. Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1. Preferred examples of these catalysts include  $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(PF_6)_2$ ,  $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_2$ ,  $Mn^{IV}_4(u-O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$ ,  $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_3$ ,  $Mn^{IV}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(OCH_3)_3(PF_6)$ , and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

#### Enzymes

**[0025]** Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme prepara-

tion. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

Amylases include, for example,  $\alpha$ -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-OS-2,247,832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

[0026] Other components which are commonly used in detergent compositions and which may be incorporated into the detergent tablets of the present invention include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, brighteners, suds suppressors, fabric softeners, dye transfer inhibition agents and perfumes.

#### Method of Washing

[0027] It is known to place traditional laundry detergent tablets in the washing drum together with the laundry. However, this method tends to result in unsightly residues appearing visibly at the window, especially in certain types of washing machine which have been designed to operate with a lower water consumption. In extreme cases visible residues can also be left on clothes at the end of the wash cycle due to non complete dissolution. The present invention also relates to a method of washing which significantly avoids this problem. The new method comprises preparing an aqueous solution of a laundry detergent for use in a washing machine, wherein the aqueous solution of laundry detergent is formed by dissolving in water a tablet formed by compressing a particulate material, the tablet comprising a surfactant and a hydrotrope compound, the hydrotrope compound having a cohesive effect on the particulate material

In a preferred embodiment according to the invention, the method more specifically relates to the preparation of an aqueous solution of a laundry detergent for use in a front-loading washing machine, the front-loading washing machine having a dispensing drawer and a washing drum, wherein the aqueous solution of laundry detergent is formed by dissolving a detergent tablet in water, characterised in that the detergent tablet is placed in the dispensing drawer and water is passed through the dispensing drawer so that the tablet is dispensed as an aqueous solution of a laundry detergent, the aqueous solution subsequently being passed in the washing drum.

## EXAMPLES

Base particulate material composition:

[0028]

	Composition A (% per weight)
Anionic Agglomerates 1	21.45
Anionic Agglomerates 2	13.00
Cationic Agglomerate	5.45
Layered Silicate	10.8
Sodium percarbonate	14.19
Bleach activator agglomerates	5.49
Sodium carbonate	13.82
EDDS/Sulphate particle	0.47
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.73
Soil Release Polymer	0.33
Fluorescer	0.18
Zinc Phthalocyanide sulphonate encapsulate	0.025
Soap powder	1.40
Suds Suppressor	1.87
Citric acid	7.10
Protease	0.79
Lipase	0.26
Cellulase	0.22
Amylase	1.08
Binder Spray-on-system	1.325
TOTAL	100.00

[0029] Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate.

[0030] Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate.

[0031] Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate.

[0032] Layered silicate comprises of 95% SKS 6 and 5% silicate.

[0033] Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

[0034] Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N, N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

[0035] Zinc phthalocyanine sulphonate encapsulates are 10% active.

[0036] Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

[0037] Binder spray-on system comprises of 50% Lutensil K-HD 96 and 50% PEG (polyethylene glycol).

[0038] Example 1 (Comprising a hydrotrope having a cohesive effect on the particulate material)

i) A detergent base powder of composition A (see table above) was prepared as follows: all the particulate material of base composition A were mixed together in a mixing drum to form a homogenous particulate mixture. During this mixing the spray-ons were carried out.

ii) 97 parts of base powder of composition A was mixed in a mixing drum with 3 parts of sodium di isoalkylbenzene sulphonate (hydrotrope having a cohesive effect on the particulate material).

iii) Tablets were then made the following way: 50 g of the mixture was introduced into a mould of circular shape with a diameter of 5.5 cm and compressed to give a tablet tensile strength (or diametrical fracture stress) of 15 kPa. The force required to obtain a tablet tensile strength of 15 kPa was 2400 N. The tablet height was 1.94 cm.

iv) The level of residue in the dispenser of a washing machine was assessed by means of the "Tablet Dispensing Test". Two laundry tablets are placed into a Baucknecht WA9850 dispenser. The water supply to the washing machine is set to a temperature of 20 °C and a hardness of 21 grains per gallon, the dispenser water inlet flowrate is set to 8 l/min. The level of tablet residues left in the dispenser is checked by switching the washing on and the wash cycle set to wash program 4 (white/colors, short cycle). The dispensing percentage residue is determined as follows:

$$\% \text{ dispensing} = [(\text{residue weight}) \times 100]/(\text{original tablet weight})$$

The % dispensing is shown in the table "Dispensing Residues".

#### Example 2 (hydrotrope)

##### [0039]

i) The same composition A was prepared following the same process as in Example 1.

ii) 97 parts of base powder of composition A was mixed in a mixing drum with 3 parts of sodium toluene sulphonate (hydrotrope).

iii) Tablets were then made following the same way as described in Example 1. The force required to obtain a tablet tensile strength of 15 kPa was 3100 N. The tablet height was 1.88 cm.

iv) The level of residue in the dispenser of a washing machine was assessed following the same procedure as described in Example 1. The % dispensing is shown in table "Dispensing Residues".

#### Example 3 (compound having a cohesive effect on the particulate material)

##### [0040]

i) The same composition A was prepared following the same process as in Example 1.

ii) 97 parts of base powder of composition A was mixed in a mixing drum with 3 parts of sodium dodecylbenzene sulphonate (compound having a cohesive effect on the particulate material).

iii) Tablets were then made following the same way as described in Example 1. The force required to obtain a tablet tensile strength of 15 kPa was 2600 N. The tablet height was 1.95 cm.

iv) The level of residue in the dispenser of a washing machine was assessed following the same procedure as described in Example 1. The % dispensing is shown in table 3.

Results:

Dispensing Residues Table:

[0041]

	Example 1	Example 2	Example 3
Compression force (N)	2400	3100	2600
Tablet height (cm)	1.94	1.88	1.95
Dispensing residues (%)	24.2	98.8	68.8

[0042] Example 4 of a tablet according to the invention:

i) A detergent base powder of composition B was prepared as follows: all the particulate materials of base composition B were mixed together in a mixing drum to form a homogenous particulate mixture. During this mixing the spray-ons were carried out. After the spray-on the sodium di isalkylbenzene sulphonate (=DIBS) was added to the rest of the matrix.

ii) Tablets were then made the following way. 43 g of the mixture was introduced into a mould of circular shape with a diameter of 5.5 cm and compressed to give a tablet tensile strength (or diametrical fracture stress) of 15 kPa.

iii) The dispensing percentage residue of the 43g tablet was of less than 15%.

	Composition B (%)
Anionic agglomerates 1	9.1
Anionic agglomerates 2	22.5
Nonionic agglomerates	9.1
Cationic agglomerates	4.6
Layered silicate	9.7
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	7.27
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.6
Soil Release Polymer	0.3
Fluorescer	0.2
Zinc Phthalocyanine sulphonate encapsulate	0.03
Soap powder	1.2
Suds suppressor	2.8
Citric acid	5.5
Protease	1
Lipase	0.35
Cellulase	0.2
Amylase	1.1

(continued)

		Composition B
		(%)
Binder spray system		
Perfume spray		3.05
DIBS		0.5
		2.1

- [0043] Anionic agglomerates comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate
- [0044] Anionic agglomerates comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate
- [0045] Nonionic agglomerates comprise 26% nonionic surfactant, 6% Lutensil K-HD 96, 40% Sodium acetate anhydrous, 20% carbonate and 8% zeolite.
- [0046] Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate
- [0047] Layered silicate comprises of 95% SKS 6 and 5% silicate
- [0048] Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.
- [0049] Ethylene diamine N-succinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N, N-disuccinic acid sodium salt, 12% of sulphate and 19% water.
- [0050] Zinc phthalocyanine sulphate encapsulates are 10% active.
- [0051] Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.
- [0052] Binder spray-on system comprises of 0.5 parts of Lutensil K-HD 96 and 2.5 parts of PEGs
- [0053] The following experiment was also carried out, whereby dissolution of a non-tablet granular material was tested with and without a hydrophobic compound, i.e. DIBS:
- [0054] Detergent of composition C was prepared as follows: all the particulate materials except for the dried zeolite were mixed together in a mixer to form a homogeneous particulate mixture. During this mixing the spray-ons were carried out. After the spray-ons the dusting was carried out with the dried zeolite.

Table 1:

Detergent base powder composition		
		Composition C
		(%)
Anionic agglomerates 1		32
Cationic agglomerates		
Layered silicate		5
Sodium percarbonate		11.5
Bleach activator agglomerates		16.2
Sodium carbonate		4.7
Sodium bicarbonate		3.76
Sodium sulphate		2.0
EDDS/Sulphate particle		2.4
Tetrasodium salt of Hydroxyethane Diphosphonic acid		0.5
Soil Release Polymer		0.8
Fluorescer		0.3
Zinc Phthalocyanine sulphate encapsulate		0.1
		0.02
Suds suppressor		2.1



Table 1: (continued)

Detergent base powder composition		
		Composition C
		(%)
Citric acid		2
Protease		0.7
Lipase		0.2
Cellulase		0.2
Amylase		0.6
Perfume encapsulates		0.2
Polymer particle		3
Perfume spray-on		0.35
Nonionic spray-on system		5.17
Zeolite		6.2

[0055] Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

[0056] Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

[0057] Layered silicate comprises of 95% SKS 6 and 5% silicate

[0058] Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

[0059] Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N, N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

[0060] Zinc phthalocyanine sulphonate encapsulates are 10% active.

[0061] Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

[0062] Perfume encapsulates comprise 50% perfume and 50% starch.

[0063] Polymer particle comprises 36%, 54% zeolite and 10% water

[0064] The Nonionic spray-on system comprises of 67% C12-C15 AE5 (alcohol with an average of 5 ethoxy groups per molecule) 24% N-methyl glucose amide and 9% water.

[0065] 150 grams of this granular detergent of composition C was introduced in the dispensing drawer of a "Hotpoint" washing machine. The water supply of the washing machine was set at a temperature of 20°Celsius and a hardness of 21 grains per gallon, at a flow rate of 2 litres per minute. After two minutes, 38 grams of the detergent composition C was remaining undissolved in the dispensing drawer.

[0066] 145 grams of this granular detergent of composition C was mixed with 5 grams of DIBS. This granular mixture was introduced in the dispensing drawer of a "Hotpoint" washing machine. The water supply of the washing machine was set at a temperature of 20°Celsius and a hardness of 21 grains per gallon, at a flow rate of 2 litres per minute. After two minutes, 30 grams of the detergent composition C was remaining undissolved in the dispensing drawer.

#### Claims

1. A tablet formed by compressing a particulate material, the particulate material comprising a surfactant and a hydrotrope compound, the hydrotrope compound having a cohesive effect on the particulate material.
2. A tablet according to claim 1, whereby at least 1% per weight of the tablet is formed from the hydrotrope compound, preferably at least 2% per weight.
3. The tablet according to claim 1, whereby the hydrotrope compound comprises sodium di isoalkylbenzene sulphonate.
4. A tablet according to claim 1, whereby the tablet has a tensile strength of more than 5 kPa, and preferably of less than 300 kPa.

5. A tablet according to claim 1, whereby the tablet is compressed using a force of less than 100000 N.
6. A tablet according to claim 1, whereby the tablet contains at least 5% per weight of surfactant.
- 5 7. A tablet having a tensile strength of at least 15 kPa for preparing an aqueous solution of a laundry detergent, the tablet giving less than 40% per weight residue in the dispenser at the end of the water supply cycle under dispensing test. the dispensing test consisting of two tablets, each tablet weighing 50g, being placed in the dispenser of a Baucknecht® WA9850 washing machine, the water supply to the washing machine being set at a temperature of 20°C and a hardness of 21 grains per gallon, the dispenser water inlet flow rate being set to 8 l/min, the machine  
10 being set to program 4 (white/colors, short cycle) and switched on.
8. A coated tablet, whereby the non-coated tablet is according to any of the above claims.
- 15 9. A method of preparing an aqueous solution of a laundry detergent for use in a washing machine, wherein the aqueous solution of laundry detergent is formed by dissolving in water a tablet formed by compressing a particulate material, the tablet comprising a surfactant and a hydrotrope compound, the hydrotrope compound having a cohesive effect on the particulate material.
- 20 10. A method according to claim 9, the tablet having a density of at least 0.9 g/cc, preferably of less than 2 g/cc.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 87 0152

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 9601 Derwent Publications Ltd., London, GB; Class D25, AN 96-007117 XP002005055 & JP 07 286199 A (LION CORP) , 31 October 1995 * abstract *	1,6	C11D17/00 C11D3/34
A	---	2,3,6	
X	GB 1 077 067 A (UNILEVER) 26 July 1967	1,2,6	
A	* claims: examples; tables 1,2 *	3-5,7	
A	---		
A	WO 93 15180 A (HENKEL KGAA) 5 August 1993	1-3,10	
	* page 2, paragraph 3; claims 1,4 *		
A	---		
A	DE 196 11 013 A (HENKEL KGAA) 25 September 1997	1,9,10	
	* page 3, line 21 - line 24; claims 1-9 *		
A	---		
A	EP 0 846 756 A (PROCTER & GAMBLE) 10 June 1998	1,4-8	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	* page 4, line 11 - line 56; claims *		C11D
A	---		
A	EP 0 225 658 A (AKZO NV) 16 June 1987	1	
	* abstract; claims *		
	-----		
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		7 December 1998	Grittern, A
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPF FORM 1503 (03/92) (Rev.03/91)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 87 0152

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-12-1998

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 1077067	A		NONE		
WO 9315180	A	05-08-1993	DE	4203031 A	05-08-1993
DE 19611013	A	25-09-1997	WO	9734994 A	25-09-1997
EP 0846756	A	10-06-1998	AU	5443698 A	29-06-1998
			WO	9824873 A	11-06-1998
EP 0225658	A	16-06-1987	DK	537986 A	13-05-1987

EPO FORM P/489

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82